

DEASPHALTING OF NON-CONVENTIONAL RESIDUES

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INTRODUCTION

Mitchell and Speight¹ established a correlation between the weight of asphaltenes precipitated from Athabasca bitumen and the solubility parameter of the precipitating solvent. The polynuclear aromatic systems in asphaltenes isolated from Athabasca bitumen was also reported by Speight². Recently, Kokal et al.³ measured precipitation of asphaltenes in Canadian heavy oils by injecting light hydrocarbon gases, e.g., methane, propane, ethane/propane mixtures, and carbon dioxide at various temperatures and pressures. A thermodynamic model proposed by Hirshberg et al.⁴ based on Flory-Huggins theory was used to correlate the experimental data and predict precipitate formation. The objective of this study was to evaluate the viability and processability of deasphalted oils (DAO) from Canadian non-conventional residues as feedstocks to produce transportation fuels. This paper only describes and compares the deasphalting characteristics of two vacuum tower bottoms (VTB) derived from Athabasca oil sand bitumen and Lloydminster heavy oil.

EXPERIMENTAL

The Athabasca VTB was obtained by distillation (ASTM D1160) of a coker feed (305°C+) from a commercial plant which produces synthetic crude from oil sand bitumen. The VTB (544°C+) constituted 63.5 wt % of the coker feed. Lloydminster VTB was obtained from an Eastern Canadian refinery that processes pipeline quality Lloydminster crude oil.

The equipment used for the deasphalting experiments is shown in Fig. 1. VTB was first dissolved in toluene (approximately 0.3 mL VTB/mL toluene). The blend was transferred to a double-ended sample cylinder (transfer vessel) which could withstand 500 psi pressure through mercury compression. The required amount of blend was transferred by mercury displacement to a detachable PVT cell which was held at 75°C. The PVT cell was removed from the system and attached to a vacuum line. Toluene was evaporated from the blend overnight. The PVT cell was restored to the deasphalting system. The volume of solvent required to give the desired solvent/VTB ratio was determined using Starling's tabulations⁵. This volume was added to the PVT cell, again using the mercury displacement technique. The cell was then brought to operating temperature and pressure, and the mixture was equilibrated by shaking for 1 h. The phases were allowed to separate for 3 h at equilibrium temperature and pressure.

The solvent-rich phase was removed at equilibrium pressure from the cell by mercury displacement and was collected in a tared flask which was chilled to prevent solvent loss (propane required a dry ice-acetone slurry, n-butane and n-pentane required dry ice, while an ice bath was sufficient for n-heptane). Toluene (50 mL) was added to the cell. After shaking for 20 min, the toluene

fraction was displaced from the cell using the mercury pump. This washing procedure was repeated four times. The weight of the solvent-rich phase was determined before the solvent was evaporated off and the weight of deasphalted oil determined. Toluene was also evaporated from the solvent-lean phase in order to determine the weight of residue. The weight of solvent in the solvent-lean phase was obtained by subtracting the weight of solvent in the solvent-rich phase from the total weight of solvent added to the cell.

To complete the phase behaviour measurements, the concentrations of the oils, resins and asphaltenes in the solvent-rich and solvent-lean phases were required. The DAO and the residue were deasphalted using ASTM method D3279 and the recovered maltene fractions were then separated into oils and resins on an Attapulugus clay column. For this study, 33 g of clay was used to separate 1 g of maltenes dissolved in 10 mL of n-heptane. The oil was eluted from the column using 200 mL of n-heptane. Resins adsorbed by the column were then eluted using 70 mL of methylene chloride followed by 70 mL of 20% diethylether in methylene chloride. All solvents were finally evaporated off.

For both VTB's, most of the phase behaviour measurements were made over a wide range of solvent/VTB ratios using the following solvents and conditions:

Propane	75°C	465 psia
n-Butane	120°C	415 psia
n-Pentane	160°C	365 psia
n-Heptane	75°C	65 psia

Several measurements were made at other conditions. In all cases the system pressures were selected so that the solvent would be undersaturated by at least 50 psia (i.e., 50 psia above the bubble point) at the desired operating temperature to ensure that the systems would remain completely in the liquid phase.

The two VTB's were characterized using ASTM and other analytical methods.

RESULTS AND DISCUSSION

Table 1 gives the analyses of the two VTB's. It can be seen that the Athabasca VTB is significantly heavier than the Lloydminster. The Athabasca contains approximately one quarter more sulphur, nitrogen, asphalt (asphaltenes + resins), Conradson Carbon residue, and 1.5 times the Ni + V content. In addition, the Athabasca VTB has much higher softening point and viscosity. The gas chromatograph distillation (GCD) data indicate that the Athabasca sample has been cut a little heavier than the Lloydminster.

Comparison of the phase behaviour for solvent-VTB systems is facilitated by plotting the phase data on pseudo-ternary phase diagrams. Typical examples are shown in Fig. 2 and 3 for n-pentane/Athabasca and n-pentane/Lloydminster systems, respectively, at 160°C and 365 psia. The dotted dilution line connecting the pure solvent apex and VTB composition on the baseline serves to indicate (i) the solvent/VTB ratio; (ii) the ratio of solvent-rich and solvent-lean phases when used together with the individual tie-line in the immiscible region.

Variables that significantly affect the phase behaviour of the deasphalting process would be expected to influence both the quantity and quality of DAO produced. Using data from the phase behaviour measurements, these effects can be investigated and are summarized as follows:

A. Effect of Solvent

Table 2 compares data for the runs conducted at 75°C with a nominal volumetric solvent/VTB ratio of 9 for various solvents. The overall weight per cent of the original VTB recovered as deasphalted oil in the upper phase increased rapidly with higher carbon number of the solvent. This was accompanied by higher recoveries of (i) the oil fraction which reached about 90 wt % with n-heptane; (ii) the resin fraction and (iii) the asphaltene fraction with n-heptane. These observations accord with the conclusions of the Flory-Huggins liquid model, i.e., increasingly heavier solvents give smaller regions of immiscibility with shorter tie-lines and heavier deasphalted oils (greater resin and asphaltene contents).

In addition, between the two VTB's there was markedly better recovery of oil and resins from the Lloydminster over the Athabasca at equivalent conditions, especially with lighter solvents. This certainly reflects the differences in the VTB constituent fractions of the two oils and their influence on the phase behaviour.

B. Effect of Temperature-Pressure

These two variables could be combined so far as the pressure at any selected temperature was kept at least 50 psia above the solvent bubble pressure to maintain a liquid system. The effect of the temperature-pressure combination is presented in Table 3 for n-butane and n-pentane at a nominal volumetric solvent/VTB ratio of 9. It can be seen that the overall recovery of VTB as DAO was lower at higher temperature. For n-butane, the recovery of both oil and resin fractions was depressed at more severe operating conditions whereas for n-pentane the major effect was to lower the recovery of the resin fraction. The results concur with Flory-Huggins model which indicates an increase of disparity between solvent and solute as the temperature is raised. This leads to a larger region of immiscibility with a broader two-phase envelope and longer tie-lines on a pseudo-ternary representation.

It should also be noted from the results that the effect of the solvent predominated over that of the temperature-pressure combination. For n-pentane at the most severe conditions, recoveries exceeded those for n-butane at the lowest temperature. Also, the recoveries of Lloydminster VTB, both overall and for individual fractions, were better than those of Athabasca VTB at comparable operating conditions.

C. Effect of Solvent/VTB Ratio

Data for the deasphalted oil composition and weight per cent extracted as a function of solvent/VTB ratio are given in Table 4 for the n-pentane/Athabasca VTB system at 160°C and 365 psia. Over a range of ratio from 20 to 5.2, there was little change in either the composition or the extracted weight of the deasphalted oil. Only as the phase envelope started to close at the lower solvent/VTB ratios, a rapid increase occurred in the asphaltenes at the expense of the oil. The overall weight extracted also showed an increase at the low solvent/VTB ratio.

To conclude, deasphalting parameters such as solvent type, temperature, pressure and solvent/VTB ratio should be optimized to make deasphalting a viable process for subsequent fuel production. The qualities of the deasphalted oils produced from this study have been partially reported elsewhere⁶. The presence of asphaltenes, and to a lesser extent resins, in the DAO will certainly reduce its desirability as a fluid catalytic cracking (FCC) feed. This has been confirmed by microactivity tests (MAT) and kinetic riser simulations which indicate that propane and n-butane deasphalted heavy oil residues are acceptable feeds for FCC riser units provided the unit is flexible enough to permit considerable increase in the regenerator operating temperature⁶. Alternatively, the n-C4 to n-C7 DAO's can be diluted with conventional gas oils or hydrotreated to yield feedstocks acceptable to unmodified FCC units as suggested by Bousquet et al.⁷

References

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Table 1. Characteristics of Feedstocks

	Athabasca VTB	Lloydminster VTB
API Gravity	-0.7	6.3
Softening Point, °C	66	36
Pen @ 25°C, 0.1 mm	11	192
Viscosity @ 135°C, cSt	2002	205
Conradson Carbon, wt %	24.3	18.3
Total Nitrogen, ppm	6390	4964
Basic Nitrogen, ppm	1820	1352
Total Sulphur, wt %	5.9	4.5
Ni, ppm	130	84
V, ppm	310	189
Fe, ppm	470	510
Cu, ppm	0.8	0.1
Na, ppm	64	< 1
Oil Fraction, wt %	46.0	59.0
Resin Fraction, wt %	36.7	27.3
Asphaltenes (n-C7), wt %	17.3	13.7
Boiling Range by GCD, °C		
IBP	331	316
5%	507	429
10%	535	465
30%	-	554

Table 2. Effect of Solvent on Deasphalting

Nominal volumetric solvent/VTB ratio - 9, Temperature - 75°C

Solvent Pressure, psia	Wt % Recovery of VTB Components as DAO			
	C3 465	n-C4 205	n-C5 105	n-C7 65
<u>Athabasca</u>				
Overall	11.6	47.1	66.0	80.5
Oil	22.2	74.8	85.5	89.6
Resins	3.7	34.4	72.5	95.0
Asphaltenes	0.1	0.3	0.4	25.6
<u>Lloydminster</u>				
Overall	27.3	64.5	77.1	
Oil	41.7	83.0	89.8	
Resins	9.8	56.7	88.1	
Asphaltenes	0.1	0.5	0.6	

Table 3. Effect of Temperature-Pressure on Deasphalting

Nominal volumetric solvent/VTB ratio - 9

Solvent	Wt % Recovery of VTB Components as DAO			
	n-C4		n-C5	
Temperature, °C	120	75	160	75
Pressure, psia	415	205	365	105
<u>Athabasca</u>				
Overall	39.2	47.1	58.4	66.0
Oil	65.5	74.8	85.7	85.5
Resins	24.6	34.4	51.4	72.5
Asphaltenes	0.2	0.3	0.7	0.4
<u>Lloydminster</u>				
Overall	56.9	64.5	71.7	77.1
Oil	76.1	83.0	93.9	89.8
Resins	43.8	56.7	59.4	88.1
Asphaltenes	0.4	0.5	0.5	0.6

Table 4. Effect of Solvent/VTB Ratio on Deasphalting

Athabasca VTB, n-Pentane, 160°C, 365 psia

Solvent/VTB w/w	Wt %					
	37.1	20.0	6.8	5.2	1.0	0.9
Oils	58.5	65.6	64.0	67.5	53.7	46.8
Resins	40.9	34.4	35.9	32.3	38.9	38.3
Asphaltenes	0.6	0.0	0.1	0.2	7.4	14.9
VTB Recovery	65.8	62.3	59.3	58.4	65.5	68.0

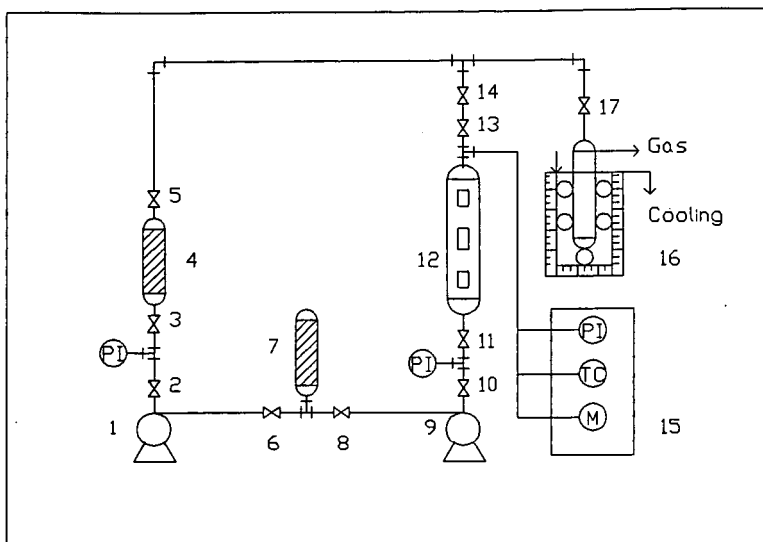


Fig. 1. Deasphalting System.

- 1: Sample pump.
- 2, 3, 5, 6, 8, 10, 11, 13, 14, 17: On-off valves.
- 4: Sample cylinder (transfer vessel).
- 7: Mercury reservoir.
- 9: Cell pump.
- 12: Three window PVT cell.
- 15: Controllers (pressure indicator, temperature control, motor control).
- 16: Solvent trap.

